

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

METHODS FOR THE REMOVAL OF ORGANIC NITROGEN, ORGANIC AND  
INORGANIC CONTAMINANTS FROM AN AQUEOUS LIQUID

USSN: 10/543,090  
PCT Filed: January 15, 2004  
Art Unit: 1797  
Applicant: Teoh Eng Chye et al  
Examiner: Allen, Cameron J.

ASSISTANT COMMISSIONER OF PATENTS  
WASHINGTON, DC 20231

Sir:

Declaration of Teoh Eng Chye Under 37 CFR §1.132:

I am a joint inventor of the present invention, disclosed in U.S. Patent Application 10/543,090. I wish to respond to the objections in the Final Office Action of the Examiner dated 6<sup>th</sup> Jan 09 by making the following comments:

SU 923961 Mamontov (herein after referred to as Mamontov) teaches a method for *removing aliphatic amines and their salts from waste by adjusting the pH to 2 – 5 with carbonic or nitric acid and heating with an alkaline or alkaline earth metal nitrite in the presence of halide ions, resulting in the evolution of nitrogen.* (Abstract).

SU 923961 may be distinguished from the present application in that it confines itself to the *removal of only aliphatic amines and their salts* only whereas claim 9 of the present application goes further in its usage in that it **removes nitrogen from a wider range of nitrogen-based organic contaminants** such as aromatic and aliphatic amines, ureas, amides and amino acids, and it also removes any residual oxidizable organic and inorganic contaminants or by-products from the nitrosonium ion reaction.

Secondly, the use of the nitrosonium ion generator in the initial stage of claim 9 is actually a controlled partial oxidation of organic nitrogen to solely nitrogen gas and not to higher oxidation state such as nitrates or nitrites (which is soluble in water). Nitrates and nitrites increase the microbial growth and BOD of the waste water.

The second stage oxidation also lowers the residual oxidizable organic and inorganic contaminants, thereby lowering the overall chemical oxygen demand (COD) of the resulting solution. The sequence of our oxidation process has to be followed to achieve the desired result; otherwise the nitrogen content in the resulting treated solution will not be lowered. The applicant is grateful for the examiner's indication that Mamontov does not teach oxidizing the aqueous liquid. The process as described by Mamontov confined to the destruction of only the aliphatic amine group through the evolution of nitrogen and the use of the Fenton's reagent (as used in US 5,716,528 Jasmin K S, et al) with Mamontov would have increase the amount of byproducts and produced nitrates in the treated liquid and therefore the nitrogen content is not reduced. The sequential oxidation stages in claim 9 not only lowers and removes the nitrogen content but also the other oxidizable organic and inorganic

contaminants in the aqueous liquid and it does not employ an absorption process with activated carbon. This further differentiates claim 9 from Jasim US 5,716,528

Thirdly, Mamontov requires the presence of halide ions for his reaction whereas the present process only requires nitrosonium ions to be present in the first stage of the reaction. The presence of halides is not necessary nor is it detrimental to the reaction in the more environmentally friendly process of the current application.

Fourthly the process described by Mamontov requires the adjustment of pH first, therefore converting the amines to aminium ( $\text{-NH}_3^+$ ) ion or the salt before heating with an alkaline or alkaline earth nitrite while the present process only requires the direct reaction of the amine with nitrosonium ions (claim 9).

Nitrous acid or a nitrite with an acid (any mineral or organic acid) is used as the nitrosonium ions generator (claim 10) because of simplicity and cost reasons. A nitrite in an acidic media as in claim 10 means that the nitrite may be added before, after or together with the acid; therefore it does not restricts the sequence of addition. Mamontov process requires an inflexible sequence. However, nitrosonium ions may also be generated by a number of ways such as dissolving nitrosonium salts (such as nitrosonium bisulfate,  $\text{NOHSO}_4$ ,  $\text{NOBF}_4$ ,  $\text{NOCIO}_4$ ,  $\text{NOSbF}_6$ ,  $\text{NOSbCl}_6$ ,  $(\text{NO})_2\text{PtCl}_6$ ,  $\text{NOAsF}_6$ ) or the reaction of dinitrogen tetra oxide,  $\text{N}_2\text{O}_4$ , and dinitrogen trioxide,  $\text{N}_2\text{O}_3$  with sulfuric acid. Iron also catalyzes nitric oxide, NO gas to nitrosonium ion which may then be used for the reaction of this application. The process in the present application does not only limit the use of the type of reactants to nitrous acid or nitrite in acid but any nitrosonium ions generator including and not restricted to those suggested above whereas SU 923961 process only specifies the use of alkaline or alkaline earth nitrites, carbonic or nitric acid and a halide.

Lastly, the acids used in SU 923961 are carbonic acid and nitric acid (an oxidizing acid) while the acid used in Claim 9 of the present application may be any mineral acid (e.g. sulfuric, phosphoric acid, hydrochloric acid, boric acid, hydrofluoric and hydrobromic acid, etc) or any organic acid (e.g. formic, acetic, propanoic and lactic acid, etc).

Mamontov did not disclose that nitrosonium ion nor nitrous acid (as nitrosonium ion generator) was the reactant used in the process and therefore one cannot assume nor arrive at that conclusion just because nitrite was used under the acidic condition of pH2-5. For the reasons given above, the applicant submits that Mamontov fails to disclose each and every feature of claim 9 and as such claim 9 is clearly innovative and patentable.

US 2004/0104181 A1, Shiota et al. (herein after referred to as Shiota) teaches a method for the catalytic wet oxidation or decomposition of organic and inorganic oxidizable substances in waste water in the liquid phase *under pressure* and at a temperature of 50 to 170 C, by using an *oxygen containing gas as an oxidant* in the presence of a specialized catalyst.

Shiota also stated that the specialized catalyst contained

- a) *activated carbon which acts as a carrier*
- b) first component from at least one from this group of metals Ti, Zr, Hf, Nb, Ta, Fe, Co, Mn, Al, Si, Ga, Ge, Sc, Y, La, Ce, Pr, Sr, Ba, In, Sn, Sb, Bi and
- c) a second component from a group consisting of Pt, Pd, Rh, Ru, Ir, Au.

The Examiner repeated his argument that paragraph (0063) suggests the element of "adding a peroxide solution in the presence of an activated carbon catalyst". Shiota (0063) suggested that an oxidant from a list of commonly known water soluble oxidants, i.e. bromine, aqueous solution of ozone, hydrogen peroxide, nitric acid, hypochlorite, dichromate, permanganate and phosphoric acid, may be used for the preparation of their specialized complex catalyst which contains large quantities of polar groups with large oxygen/carbon ratio. Thereafter these oxidants are no longer employed. The distinction is important because the step with the peroxide is precursor step prior to the use of the catalyst. Shiota uses the specialized complex catalyst in the oxygen containing gas oxidation to treat the contaminants in waste water.

Shiota (0073 and 0074) heat treats the specialized complex catalyst at preferred temperature of 200 °C after depositing component (a) and again at preferred temperature of 300 °C after depositing component (b). These temperatures are way above the boiling point of liquid hydrogen peroxide (150.2 °C). Therefore it can be reasonable to conclude that any hydrogen peroxide that may be used in the preparation of the activated carbon will be completely removed from the catalyst and is not present during the oxygen containing gas oxidation.

Shiota (0064) specifically mentions that the reason for the preferable use for the activated carbon as the carrier is for its "excellent absorbability of oxidizable substances" meaning that activated carbon is used as an absorbent for his specialized complex catalyst and (0065 and 0066) even describes the characteristics for the selection of activated carbon absorbent. Therefore it clearly shows that there is no intention in using of simple activated carbon as the catalyst in Shiota.

Shiota (0009 and 0010) stated that it is *impossible to utilize activated carbon as a catalyst for wet oxidation of waste water*. The current invention totally contradicts these statements and proves that Shiota actually leads one away from the current invention.

Thirdly, US 2004/0104181 A1 maybe readily distinguished from the present invention as the process uses oxygen containing gas (air or enriched air) as the gaseous oxidant whereas liquid hydrogen peroxide is used as the liquid oxidant in the current invention.

Fourthly, the wet oxidation process as described by Shiota (0088 & claim 5) is conducted under pressure necessitating the use of a pressure vessel as the reactor. Shiota's invention has a working temperature range of 50° – 170°C (water-vapor pressure 118 psia.) and states that the most preferable working temperature (0087) is above 110° C (water-vapor pressure 20.8 psia). The oxidation process in the present invention is conducted under ambient pressure throughout the temperature range i.e. below the boiling point of water, in an unpressurized vessel because hydrogen peroxide exists in the liquid phase throughout the specified range of temperature and free radicals are formed during reaction. The physical requirements demonstrate that there are crucial differences in our processes.

The fifth point is that Shiota mentioned that his specialized complex catalyst consists of *activated carbon as a carrier* for first component from list of metals or metalloids and a second component from a list of noble metals, i.e. both components are deposited onto the carbon backbone. Another function of the *activated carbon in US 2004/0104181 A1 was as an absorbent*. The catalyst used in the current invention is only activated carbon without any additional metals or metalloid.

Based on the clear language and the properties inherent in the complex specialized catalyst of Shiota, the applicant strongly believes that Shiota expressly teaches away from the applicant's claimed invention. Therefore the applicants submit that the use of *activated carbon as a catalyst for peroxide oxidation of contaminants in aqueous solution* is neither obvious nor predictable by even those well versed in the art through the study of US 2004/0104181 A1, Shiota et al.

US 5,716,528 Jasim, et al. (herein thereafter referred to as Jasim) describes a method to remove aromatic organic contaminants in waste water by oxidizing with *hydrogen peroxide in the presence of catalytic amounts of ferrous ions at acidic pH* (the well known Fenton's reaction developed in 1890's and used for oxidizing organics before prior date) and then the oxidized water is passed through activated carbon to adsorb the residual organic contaminants.

Jasim can be distinguished from the present invention because the catalyst used in the hydrogen peroxide oxidation process is ferrous ions in the solution while the catalyst used for the peroxide oxidation in the current invention is solid activated carbon (claims 11 & 13).

Secondly the oxidation process as described by Jasmin is only possible in the acidic range below pH4 while the oxidation process in the current invention is possible in both acidic and alkali range i.e. 2-12 (claim 17).

Thirdly, there is an increase in the total dissolved salt (TDS) in the discharge water from the oxidation process by Jasim because acidic condition below pH 4 is required and also that the ferrous ions used in the needs to be removed through precipitation by adjusting the pH to 7 or above, while in the current invention there is no increase in TDS because no ionic catalyst is used.

Fourthly Jasmin (claims 6, 8(ii) & 9) described the use of activated carbon as an absorbent (a well known property for activated carbon particularly to those well versed in the art) for the residual organic contaminants while in the current invention the main purpose of the *activated carbon* is to *act as the catalyst for the peroxide oxidation process*.

Lastly the amount of activated carbon used as a catalyst for the peroxide oxidation of the present invention is far less than that required as an absorbent of residual contaminants in US 5,716,528 Jasim. Even the time in between the change of activated carbon for use as catalyst is very much longer than that when it is used as an absorbent.

Therefore the applicants submit the use of activated carbon as a catalyst for peroxide oxidation of contaminants in aqueous solution is neither obvious nor predictable by even those well versed in the art through the study of US 5,716,528 Jasim K S, et al. or even together with US 2004/0104181 A1, Shiota et al.

For further clarification, catalyst tends to be highly specific in reacting with one substance or a small set of substances for a specific reaction mechanism. A substance can act as a catalyst for one set of reaction and may also be a catalyst for another, e.g. iron acts as a catalyst in Friedel Crafts reactions, hydrogen peroxide oxidation (Fenton's reaction) and synthesis of ammonia in Haber process. It is not possible to predict the use of catalyst for one reaction or process from another e.g. Ferrous ions (Fenton's reagent) does not act as a catalyst for Shiota's oxygen oxidation process nor the metals of components 1 or 2 of Shiota's oxidation process acts as a catalyst for Fenton's oxidation process.

The examiner cited US 6,720,283 Ding et al. as prior art of claims 13, 14, 17 and 18 of the present invention.

US 6,720,283 Yunjie Ding et al. related to cobalt based catalysts that are supported by *activated carbon carrier* and the use of the catalyst for the *conversion of synthesis gas to diesel fuel* during the Fisher Tropsch process. Ding showed the method of preparation of the activated carbon supported *cobalt based catalysts* containing a *Group IVB metal promoter or Group IIIB or Group VIII metal promoter*.

US 6,720,283 may be readily distinguished from the present application in that it deals with a specialized catalyst for the synthesis of diesel fuel from synthesis gas whereas claims 13,14,17 and 18 of the present invention deals with the use of activated carbon catalyzed peroxide oxidation of organic and inorganic contaminants in aqueous phase. The reactants, reaction of the process, the phase at which it is occurring and the mechanism of both process are completely different.

Secondly the purpose of the activated carbon in US 6,720,283 is to carry the cobalt based catalyst (i.e. the backbone) while in the present invention the activated carbon acts as the catalyst for the peroxide oxidation.

Lastly the catalyst by Ding is Cobalt based with other metals while the catalyst in the present invention is activated carbon. The various ways of placing the catalyst in the reactor such that the catalyst is in continuous contact with the aqueous solution of peroxide and contaminants are clearly shown in claim 13, i.e. in fixed bed, that is solution moving through the fixed catalyst or moving bed (or suspension in solution) that is the solution moving with the catalyst or catalyst moving through the solution. However the main objective of the independent claim 13 is the use of activated carbon as the catalyst for the peroxide oxidation of organic and inorganic contaminants in aqueous solutions.

Therefore the applicants submit that the use of activated carbon as a catalyst for peroxide oxidation of contaminants in aqueous solution as in claims 13, 14, 17 and 18 is neither obvious nor predictable by even those well versed in the art through the study of US 6,720,283 Yunjie Ding et al. or even together with US 2004/0104181 A1, Shiota et al and US 5,716,528 Jasim K S, et al. Nothing in Ding cures the deficiencies in Shiota or Jasim. For at least these reasons stated, the applicant submits that the use of activated carbon as the catalyst for peroxide solution oxidation of contaminants as in claim 13 is both innovative and novel and is clearly patentable.

Combination of Citations:

The examiner cited Mamontov SU 923961 and Jasim US 5,716,528 in combination as rendering the claims 9 and 10 of the present application obvious. The applicant respectfully disagrees with this objection and notes the following:

None of the cited documents showed a controlled sequential process to remove the nitrogen and lower the chemical oxygen demand of aqueous liquid by an initial controlled oxidation using nitrosonium ion of a wide range of nitrogen based organic contaminants such as aromatic and aliphatic amines, ureas, amides and amino acids, followed by a second stage oxidation to remove any residual oxidizable organic and inorganic contaminants or by-products from the nitrosonium ion reaction.

Mamontov SU 923961 confines to the removal of only aliphatic amines and their salts by heating with carbonic or nitric acid and heating with an alkaline or alkaline earth metal nitrite in the presence of halide ions while claim 9 **removes nitrogen from wider range of nitrogen based organic contaminants** such as aromatic and aliphatic amines, ureas, amides and amino acids using nitrosonium ions generator. The nitrosonium ions may be obtained from a wide number of sources or generators such as nitrosonium salts, nitrous acid, a nitrite and an acid, or oxides of nitrogen with sulfuric acid or iron.

Jasim US 5,716,528 uses Fenton's reagent (acidified hydrogen peroxide catalyzed with ferrous ions) for the oxidation of aromatic hydrocarbon contaminants and subsequent activated carbon absorption for the residual contaminants. The two stage process, i.e. oxidation followed by absorption as shown by Jasim is totally different from the process as in claim 9 of the current application which is a double oxidation process without a subsequent activated absorption process.

Therefore the applicants submit that either alone or in combination none of the documents cited renders obvious the methods as claim in claims 9 and 10 of the present application even to one skilled in the arts.

The applicants therefore respectfully request the examiner's favorable reconsideration and withdrawal for the objections to claims 9 and 10.

Claims 11 - 12 stand rejected over Mamontov and further in view of Shiota. The applicant respectfully traverses this rejection. Claims 11 - 12 depend on claim 9 which is allowable over Mamontov in view of Jasim for reasons discussed above. Nothing in Shiota cures the deficiencies of Mamontov and Jasim.

The examiner cited Shiota et al. US 2004/0104181, Ding et al. US 6,720,283 and Jasim US 5,716,528 in combination as rendering claims 13, 14, 17 and 18 of the present application obvious. The applicant respectfully disagrees with this objection and notes the following:

All the cited documents use the activated carbon either as a carrier or as an absorbent while use of the activated carbon in the process of the current application is as a catalyst for the peroxide oxidation both organic and inorganic contaminants.

The liquid phase activated carbon catalyzed peroxide oxidation of the organic and inorganic contaminants is pH tolerant because the catalyst is in the solid state unlike ionic ferrous ions

in acidic pH (below pH 4) in Jasmin US 5,716,528. Shiota et al. US 2004/0104181 pressurized oxygen containing gas oxidation process is a totally different oxidation process to the aqueous phase peroxide oxidation under ambient (atmospheric) pressure because the activated carbon catalyzed oxidant remains in the liquid phase throughout the temperature range. The activated carbon peroxide oxidation process of the current application is also totally and absolutely different from the process as described in Ding et al. US 6,720,283 in all matters concerning a chemical reaction, reactants, mechanism, process, products, conditions and equipment usage.

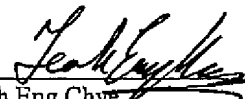
The applicants submit that a wide variety of species of substances (for example ferrous ions) may be present in the waste water; however such species takes no part in the mechanism by which the present invention operates.

Therefore the applicants submit that either alone or in combination none of the documents cited renders obvious the methods as claim in claims 13, 14, 17 and 18 of the present application even to one skilled in the arts.

The applicants therefore request the examiner's favorable reconsideration and withdrawal for the objections to claims 13, 14, 17 and 18. We look forward to receive the examiner's reply.

I hereby declare that all statements made herein are true, and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully Submitted,

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Teoh Eng Chye